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Photosensitized Transformations Involving Electronic Energy Transfer in Natural Waters: Role of Humic Substances

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16. ABSTRACT

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Photosensitized Transformations Involving Electronic Energy Transfer in Natural Waters: Role of Humic Substances

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■ Studies are reported of the kinetics of photosensitized reactions involving the transfer of absorbed light energy from humic substances to various trace organic chemicals in water. The photoisomerization of 1,3-pentadiene and the photooxygenation of 2,5-dimethylfuran were used to probe the nature and concentrations of the excited species that mediate humus-sensitized photoreactions of aquatic pollutants. Evidence is presented that the photosensitized reactions of pentadiene and dimethylfuran do not involve binding of the chemicals by the humic substances. Kinetic results indicate that the key steps in both photoreactions involve the transfer of electronic energy from triplet states of the humic substances. Up to half of these triplets are estimated to have energies of at least 250 kJ/mol, sufficiently high to transfer energy to polycyclic aromatic hydrocarbons, nitroaromatic compounds, conjugated dienes, and other types of chemicals. Steady-state concentrations of the humus-derived triplets are estimated to typically fall in the 10^{-15}–10^{-13} M range in the upper layers of sunlight-irradiated natural waters. The concentrations are proportional to UV absorption coefficients of the water. Action spectra for the photosensitized reactions indicate that solar ultraviolet radiation is most important in inducing the reactions. Results of the study are used to estimate maximum rates of reactions photosensitized by humic substances.

Introduction

As sunlight penetrates down into freshwater and coastal marine waters, the great bulk of the radiation is absorbed by natural dissolved or particulate substances. Initial studies of the influence of these natural substances on rates of photochemical and photobiological processes in aquatic environments have focused on light attenuation effects (*1*, *2*). Results of these studies have been used to predict rates of pollutant photoreactions that are initiated through direct absorption of sunlight by the pollutant (*1*).

A number of recent investigations have shown that the influence of natural substances on photoreactions in freshwaters and seawater is not limited to light attenuation (3–13). Sunlight-induced reactions involving free radicals may be initiated through photolysis of natural inorganic constituents such as nitrite (*3*) and hydrogen peroxide (*4*, *5*). Moreover, a significant portion of the solar radiation absorbed by freshwater humic substances results in formation of electronically excited molecules that are capable of participating in a variety of reactions with aquatic pollutants (*8–15*). These photosensitized reactions can greatly accelerate the light-induced transformation of trace chemicals in natural waters, in some cases resulting in rapid photoreaction of compounds that are stable to sunlight in distilled water (*6–13*).

Humic substances have been shown to sensitize oxygenations and other photoreactions of organic chemicals involving electronic energy transfer (*9*), but there is a dearth of information concerning factors that influence the rates of these processes in aquatic environments. In this paper, humus-sensitized photoreactions of two organic chemicals, 2,5-dimethylfuran and 1,3-pentadiene, are used to explore the nature and concentrations of the excited species that are involved in the rate-determining steps of the energy-transfer processes. Results of this study are used to define types of pollutants that may be susceptible to photosensitized reactions involving energy transfer and to estimate maximum rates of these photoreactions in natural waters.

As used in this paper, the terms "humic substances" or "humus" refer to the colored organic matter that is dissolved in natural waters or extractable from soil by base. No attempts were made to elucidate the structures of the photoactive chromophores.

Experimental Section

Materials. *cis*-1,3-Pentadiene (99%) (cP) and *trans*-1,3-pentadiene (99%) (tP) were obtained from Chemical Samples Co. and used as received. 2,5-Dimethylfuran (DMF) was obtained from Chemical Samples Co. and distilled prior to use. 2,4-Hexadien-1-ol (99%), mixed isomers, was obtained from Chemical Samples Co. and distilled prior to use. Valerophenone from Eastman was distilled before use, and *p*-nitroanisole from Aldrich

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Chemical Co. was recrystallized from 95% ethanol. Reagent-grade acetophenone from Fisher Scientific was used as received, as was a sample of *p*-(trimethylammonio)benzophenone chloride that was obtained as a gift from Dr. Richard Hautala, University of Georgia, Athens, GA. Aldrich 2,6-naphthalenedisulfonic acid disodium salt was purified by recrystallization from aqueous sodium chloride solution. The natural water samples were obtained from the top meter of water bodies and refrigerated at 5 °C prior to use. Commercial humic acids were obtained from Aldrich Chemical Co. and Fluka AG, and a commercial fulvic acid was obtained from Contech E.T.C. Ltd. A sample of humic substances isolated from Wylde Lake (Ontario) was contributed by Dr. John Carey of the Canada Center for Inland Waters. Dr. Paul Ringhand, USEPA, Cincinnati, OH, provided a sample of Ohio River fulvic acid. Spectrograde acetonitrile from Burdick & Jackson was used as received. Other chemicals used were reagent grade obtained from various commercial sources.

Preparation of Solutions for Irradiation. Procedures used for preparing solutions of the commercial humic acids and fulvic acid are described elsewhere in detail (*9*). These solutions and the natural water samples were centrifuged at 15 000 rpm for 1 h to remove particulates. For all studies in sunlight the solutions were optically matched by adjusting their absorbances to the same value at 365 nm through addition of distilled water. Aqueous stock solutions of valerophenone, *p*-nitroanisole, and the pure photosensitizers were prepared by adding to distilled water an amount of chemical that exceeded its aqueous solubility by about 10%. The resulting mixture was stirred for 24 h and then centrifuged as described above to remove undissolved chemical. The resulting stock solutions were diluted by addition of distilled water to obtain concentrations required for the irradiations.

With the exception of the irradiations of DMF solutions in the monochromator, the following procedure was used to prepare solutions for the irradiations. Aqueous solutions containing the photosensitizers and other additives were prepared in volumetric flasks. Then 8.50-mL portions of these solutions were added to 100 × 13 mm Pyrex test tubes equipped with gas-tight Mininert caps. Finally, 40 μL of a 2 mM solution of substrate (DMF, cP, or tP) was injected into the solution in each test tube, resulting in a substrate concentration of about 10 μM.

Irradiation of Samples. Three procedures were used to irradiate samples in this study: by exposure to sunlight, by exposure to monochromatic light in a "merry-go-round" apparatus, and by exposure to monochromatic light derived from a monochromator.

The procedures used in the exposures to sunlight have been described elsewhere (*9*). Dilute solutions of valerophenone (10 μM) were used as outdoor actinometers in these experiments (*16*).

The irradiations in the merry-go-round apparatus (*17*) were performed as previously described (*10*). The merry-go-round apparatus ensures that the same intensity of irradiation impinges on each sample of a set of simultaneously irradiated samples. Dilute aqueous solutions of *p*-nitroanisole were used as chemical actinometers in the experiments with 313- and 366-nm light, and ferrioxalate actinometers (*18*) were used for experiments with 405- and 436-nm light.

Wavelength studies of the humus-sensitized photoreaction of DMF were conducted using the Schoeffel Reaction Chemistry System. This apparatus is basically an optical bench that consists of a 1000-W xenon lamp, high intensity monochromator, and sample compartment. The light intensity impinging on the samples was determined on a YSI Model 65A radiometer that was calibrated vs. ferrioxalate actinometers (*18*).

For the purpose of determining the ratios of *cis*- to *trans*-pentadiene at a photostationary state, aqueous solutions containing the photosensitizers and cP or tP were irradiated for about 10 half-lives and then analyzed. The samples were irradiated for another half-life and reanalyzed to ensure that the ratio was no longer changing. The standard error observed in triplicate experiments was typically ±2% of the mean.

Equipment. Electronic absorption spectra were obtained on a Perkin-Elmer Model 356 spectrophotometer. *cis*- and *trans*-1,3-pentadiene were analyzed as previously described (*9*) on a Tracor MT-222 gas chromatograph equipped with flame detector and a 6 m long by 2 mm i.d. gas–liquid chromatographic (GLC) column packed with 20% 1,2,3-tris(2-cyanoethoxy)propane on Gas-Chrom RA. A Micromeritics high-pressure liquid chromatograph equipped with a UV detector was used to analyze the reaction mixtures containing 2,5-dimethylfuran, valerophenone, or *p*-nitroanisole. Acetonitrile–water mixtures were used as the mobile phase in a column packed with ODS-2. Dioxygen concentrations were measured by using a YSI Model 54 oxygen meter.

Procedures for Kinetic Studies. Both DMF and the pentadienes are volatile compounds in water. Therefore, all kinetic studies were conducted by using gas-tight reaction cells that were completely filled with air-saturated aqueous solutions. After introduction of the substrate to the filled test tube or cuvette, the solutions were exposed to light as described above. In the outdoor experiments three replicates of each solution and two sunlight actinometers were simultaneously irradiated, typically for a period less than 20 min. Rate constants were computed assuming that the photoreactions were described by first-order rate expressions. In the kinetic runs using the merry-go-round, a series of samples and actinometers were simultaneously irradiated with periodic removal of samples for analysis. With the monochromator, three replicates were irradiated separately, and first-order rate constants were computed from the relative change in concentration of the DMF for each replicate. The radiometer, which was monitored throughout the exposure, generally indicated no change in incident light intensity during the irradiations. Standard errors in the computed rate constants were typically ≤ ±15% of the mean value.

The kinetic studies of the influence of dioxygen and 2,4-hexadien-1-ol on the photosensitized isomerization of cP were conducted in sunlight with the humic substances and in the merry-go-round with acetophenone as sensitizer. Aqueous solutions containing the same concentrations of sensitizer but varying concentrations of quencher (including no added quencher) were prepared, and portions of each solution were added to two equivalent test tubes. After the test tubes were capped, the same amount of cP was then injected into each test tube. The test tubes were irradiated for the same length of time. Then the reaction mixtures were analyzed for cP and tP.

In all the experiments dark controls showed no loss of substrate. Also, cP, tP, and DMF did not react when irradiated as described above in air-saturated distilled water.

Action Spectra. Spectral response functions, $X_{s,\lambda}$, were computed from the kinetic data obtained at various wavelengths by using the following equation:

$$X_{s,\lambda} = k_{s,\lambda}/(I_\lambda l S_\lambda) \qquad (1)$$

where $k_{s,\lambda}$ is the first-order rate constant for the reaction

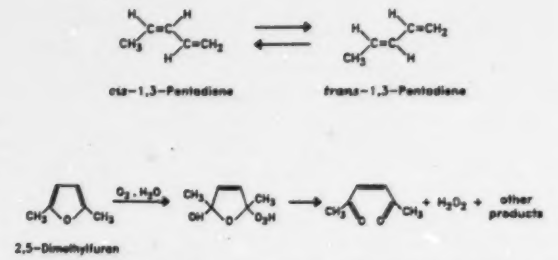

Figure 1. Photosensitized reactions of 1,3-pentadiene and 2,5-dimethylfuran in water.

of DMF, cP, or tP, I_λ is the light intensity term (number of photons that enter the reaction cell per unit time and volume), S_λ is the "light screening factor", and l is the light path length. The values of I_λ were computed from kinetic data obtained from irradiation of chemical actinometers in the same way as the solutions of DMF or the dienes. With *p*-nitroanisole (2 μM; no pyridine) as the actinometer at 313 or 366 nm, the following simple equation can be used to compute I_λ (in einsteins/(L h)):

$$I_\lambda = C_\lambda k_p / l \tag{2}$$

where k_p is the first-order rate constant for photolysis of the nitroanisole (in h^{-1}) and C_λ is a constant equal to 0.15 einstein/L for 313-nm light and 0.77 einstein/L for 366-nm light. The value of S_λ was computed by using

$$S_\lambda = (1 - 10^{-\alpha_\lambda l})/(2.303\alpha_\lambda l) \tag{3}$$

where α_λ is the decadic absorption coefficient of the solution. The mean value of the light path length l for the experiments in the merry-go-round was estimated by exposing a series of solutions containing valerophenone (10 μM) and varying concentrations of Fluka humic acid. The light screening factor S_λ was computed by assuming that the observed rate constant in the humic acid solution equalled $S_\lambda k_p$(dw) where k_p(dw) was the rate constant in distilled water. This experimental value of S_λ was used along with the absorption coefficients and eq 3 to compute the mean light path length. This procedure was validated by conducting it in the monochromator (310 nm) using a reaction cell with a path length known to be 1.00 cm.

Results and Discussion

A wealth of investigations have established that both photosensitized oxygenations (*19*) and sensitized photoisomerizations of alkenes (*20*) involve electronic energy transfer from triplet states of photosensitizers. For this study we selected the oxygenation of 2,5-dimethylfuran (DMF) and the cis–trans isomerization of 1,3-pentadiene (Figure 1) as convenient chemical processes to investigate transfer of light energy in natural waters.

2,5-Dimethylfuran and the pentadiene isomers were selected as substrates for several reasons. Experimental considerations include their relatively high water solubilities (>0.005 mol/L), their transparency to solar UV radiation and extremely low direct photolysis rates, and their great sensitivity to photosensitized reactions. In addition, convenient methods had been developed to directly analyze for DMF, cP, and tP at trace concentrations in water (*9*). Finally, both substrates have previously been studied extensively with pure photosensitizers in organic solvents, so a great deal of background information was already available concerning the kinetics of their reactions.

Rate Expressions. Young and co-workers (*21*) have previously shown that photosensitized oxygenations are first order with respect to substrate when substrate concentrations are very low. Under these conditions, which

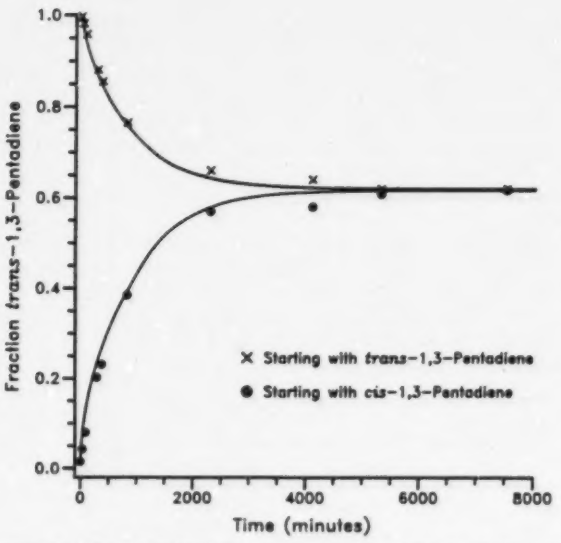

Figure 2. Kinetic data for the photosensitized isomerization of *cis*- and *trans*-1,3-pentadiene (10 μM) in a water sample from the Aucilla River.

are usually found in aquatic environments, the substrate has practically no effect on the lifetime of singlet molecular oxygen, the reactive intermediate in oxygenations (see below). In the present study, as in earlier studies (*8–10*), we found that the photooxygenation of DMF (10 μM), measured as the disappearance of substrate in irradiated solutions, was cleanly first order in all the aqueous systems that were studied. The kinetic data were generally treated by computing first-order rate constants from the concentration vs. time data; that is, $k_s = \ln (C_0/C)/t$ where C_0 represents initial DMF concentration and C represents DMF concentration after light exposure for time t.

Previous studies in organic solvents using a variety of photosensitizers have shown that the photoisomerization of cP or tP is a reversible reaction (*22*). With prolonged irradiation in the presence of a photosensitizer, isomerization proceeds until the ratio of cis to trans diene no longer changes. When this "photostationary state" is reached, the rate of cis to trans isomerization equals the rate of the reverse reaction. A typical plot of the kinetic data obtained for the photoisomerizations in natural waters is shown in Figure 2. The same photostationary state was reached starting with either cP or tP. At the concentration of diene used in this study (10 μM), the initial rate of photoisomerization was first-order with respect to diene in all the experiments. The integrated rate expression for the photoisomerization is shown in eq 4, where t_∞, t_0, and

$$\ln \frac{(t_\infty - t_0)}{(t_\infty - t_t)} = k_i t \tag{4}$$

t_t represent the fraction of the diene that was trans at the photostationary state, at time zero, and at time t. The rate constant, k_i, for the isomerization equals the sum of the rate constants for the cis–trans conversion and for the trans–cis conversion (*23*).

For the studies in sunlight, outdoor actinometers consisting of dilute valerophenone in distilled water were simultaneously irradiated. To correct for the variability in sunlight intensity, the rate constants were ratioed to the first-order rate constant for the actinometer, k_{act}, to give a relative rate constant, k_{rel}.

$$k_{rel} = k_s / k_{act} \tag{5}$$

At latitude 40°N, the value of k_{act} averaged over a full year is 0.88 h^{-1}.

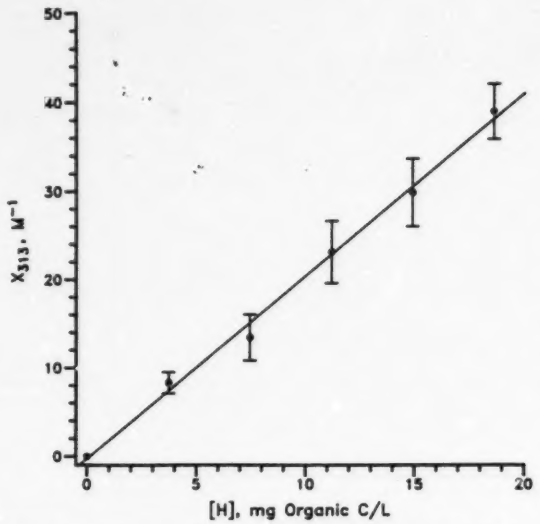

Figure 3. Dependence of response function (366 nm) for photosensitized isomerization of *cis*-1,3-pentadiene on concentration of Fluka humic acid solutions. Bars indicate standard error for five replicates.

Several previous studies have shown that humic substances are important photosensitizers in aquatic environments. Therefore, we also examined the kinetics of the DMF and diene photoreactions in aqueous solutions of humic substances that were isolated from natural waters or soils. These reactions could also be described by first-order rate expressions.

Static Photosensitization. In a recent paper, Carter and Suffet (*24*) suggested that pollutant photoreactions sensitized by humic substances may involve binding of the substrate by the dissolved humus. This possibility is depicted in eq 6, where H and P represent humus and pol-

$$H + P \underset{}{\overset{K}{\rightleftharpoons}} H\text{–}P \xrightarrow[\text{light}]{k_b} \text{products} \qquad (6)$$

lutant and H–P represents the pollutant bound (or complexed) by the humus. According to this scheme, the bound pollutant is hypothesized to be photoreactive. This mechanism, which can be referred to as "static photosensitization", can be ruled out for the substrates used in this study on the basis of several experimental results.

Under the assumption that the binding is rapidly reversible, the dependence of the response function (rate constant ratioed to average light intensity) on the concentration of humic substances, [H], should be described by the expression in eq 7, where K is the equilibrium

$$X_{s,\lambda} = \frac{Kk_b[H]}{1 + Kk_b[H]} \qquad (7)$$

constant for the binding and k_b is the rate constant for photolysis of H–P. The response function, which corrects the kinetic data for internal light filtering by the humus, is defined by eq 1. This expression requires that plots of the response function vs. [H] curve downward and eventually flatten. Such curvature was not detected in the plots of the kinetic data for the diene isomerization in natural water samples or in aqueous solutions of soil-derived humic acids or fulvic acids. A typical plot of the dependence of the response function for cP isomerization on the concentration of Fluka humic acid is shown in Figure 3. The linearity of this plot is particularly significant because humic acids have been shown to bind organic solutes more effectively than other types of humic substances (*24*).

Table I. Results Obtained from Quenching of the Photosensitized Isomerization of *cis*-1,3-Pentadiene (2.0×10^{-5} M) in Air-Saturated Aqueous Solutions by 2,4-Hexadien-1-ol

reaction medium	$k_q\tau$, M^{-1} [a]	k_q, $M^{-1}\ s^{-1}$ [b]
0.002 M acetophenone, in distilled water	$6.2\ (\pm 0.9) \times 10^3$	28×10^8
Aucilla River water sample, Lamont, FL	$1.2\ (\pm 0.1) \times 10^3$	5.4×10^8
Suwannee River water sample, Suwannee Springs, FL	$1.4\ (\pm 0.1) \times 10^3$	6.2×10^8
Aldrich humic acid, in distilled water	$0.66\ (\pm 0.06) \times 10^3$	3.0×10^8
Fluka AG humic acid, in distilled water	$2.5\ (\pm 0.3) \times 10^3$	11.0×10^8
Contech fulvic acid in distilled water	$0.89\ (\pm 0.10) \times 10^3$	4.0×10^8

[a] Slope of Stern–Volmer plot; mean of three experiments ± standard deviation. [b] Computed assuming that lifetime of all triplets equals 2.2 μs in the absence of quencher.

Table II. Effects of Oxygen Concentration on Rate Constants for Photosensitized Reactions of 2,5-Dimethylfuran and *cis*-1,3-Pentadiene[a]

	$k_{rel,DMF}$ [b]		$k_{rel,cP}$ [b]	
reaction medium	$[O_2] = 2.6 \times 10^{-4}$ M	1.2×10^{-3} M	$[O_2] = 2.6 \times 10^{-4}$ M	1.2×10^{-3} M
0.002 M acetophenone,[c] in distilled water	[d]	[d]	0.63	0.15
Aucilla River water sample, Lamont, FL	1.4	1.5	0.22	0.063
Suwannee River water sample, Suwannee Springs, FL	1.3	1.2	0.18	0.060
Wylde Lake (Ontario) humus, in distilled water	0.81	[d]	0.092	0.046
Ohio River (Cincinnati) fulvic acid, in distilled water	3.0	[d]	0.43	0.17
Fluka AG humic acid, in distilled water	1.3	1.5	0.14	0.048
Aldrich humic acid, in distilled water	1.2	1.1	0.13	0.046
Contech fulvic acid, in distilled water	1.2	1.4	0.10	0.028

[a] In sunlight except as noted. [b] Ratio of rate constant for photosensitized reaction to rate constant for valerophenone actinometer. [c] At 313 nm. [d] Not determined.

Similar results have been reported elsewhere (*10*, *13*) for photosensitized oxygenations in humus solutions. These linear plots do not rigorously exclude static sensitization, however. If only a small fraction of substrate were bound and $Kk_b[H]$ is $\ll 1$, then the response function would be proportional to [H].

Other results also are inconsistent with the involvement of static sensitization. The rate constants for the sensitized photoreactions of DMF and cP in optically matched solutions (Tables I–III) fall in much narrower range than would be expected if static sensitization were involved. Carter and Suffet (*24*) reported that equilibrium constants for the binding of DDT by various humic substances vary

Table III. Kinetic Data for Photosensitized Reactions of 2,5-Dimethylfuran (DMF) and *cis*-1,3-Pentadiene (cP) in Optically Matched Natural Water Samples and Aqueous Solutions of Humic Substances[a]

reaction medium	k_{rel}[b]		$10^{13} \times$		
	DMF	cP	$[^1O_2]$, M[c,d]	$[^3H^*] + [^3S^*]$, M[c,e]	$[^3H^*]$, M[c,f]
Aucilla River water sample, Lamont, FL	1.4	0.22	4.4	2.2	1.0
Suwannee River water sample, Suwannee Springs, FL	1.3	0.18	4.1	2.0	0.71
Wylde Lake (Ontario) humus, in distilled water	0.81	0.092	2.5	1.3	0.37[g]
Ohio River (Cincinnati) fulvic acid, in distilled water	3.0	0.43	9.4	4.7	1.8[g]
Fluka AG humic acid, in distilled water	1.3	0.14	4.1	2.0	0.31
Aldrich humic acid, in distilled water	1.2	0.13	3.8	1.9	1.0
Contech fulvic acid, in distilled water	1.25	0.10	3.8	1.9	0.61
mean values			4.6	2.3	0.84

[a] Absorbance at 365 nm equals 0.25 cm^{-1} in a 1.00-cm cell. [b] Ratio of k_s for DMF reaction or k_i for cP isomerization to photolysis rate constant for valerophenone actinometer. [c] Computed using sunlight photolysis rate constants that were estimated from k_{rel} assuming that k_{act} equals 0.88 h^{-1} (eq 5); the mean value for the valerophenone actinometer at latitude 40° N. [d] Typical near-surface concentration of singlet oxygen (eq 21). [e] Typical near-surface concentration of triplets that transfer energy to dioxygen (eq 22). [f] Typical near-surface concentration of triplets with energy 240–250 kJ/mol (eq 23). [g] Computed assuming that $k_q = 6 \times 10^8$ M^{-1} s^{-1}.

considerably, with soil-derived humic acids much more effective than dissolved organic substances in natural waters. The humic acids used in this study, however, were not found to be significantly more efficient sensitizers than the dissolved organics in the natural water samples. Finally, the UV absorption spectra of DMF and pentadiene in water were found to be unaffected by the presence of humic substances, whereas spectral changes would be likely if the humus bound these substrates.

Although static sensitization does not account for the results of this study, it may come into play with substrates that are much more hydrophobic than DMF or the pentadienes. The substrates used in this research are over one million times more water soluble than DDT, the solute used by Carter and Suffet (*24*) in their binding studies.

Scheme for Energy Transfer. On the basis of the above considerations as well as a large number of other results from previous studies of photosensitized reactions in solution (*19, 20, 22, 25*), it appears most likely that the kinetic results of this study can be described by the following scheme. This scheme depicts the key energy-transfer steps as occurring when excited sensitizer, denoted by the asterisk, and energy acceptor (substrate or dioxygen) diffuse together.

$$H \xrightarrow{\text{light}} {}^1H^* \rightarrow {}^3H^* \quad (8)$$

$${}^3H^* \xrightarrow{k_d} H + \text{heat} \quad (9)$$

$${}^3H^* + O_2 \xrightarrow{k_{ox}} H + {}^1O_2 \quad (10)$$

$${}^3H^* + Q \xrightarrow{k_q} H \quad (11)$$

$${}^3H^* + cP \xrightarrow{k_c} T + H \quad (12)$$

$${}^3H^* + tP \xrightarrow{k_t} T + H \quad (13)$$

$$T \rightarrow cP \quad (14)$$

$$T \rightarrow tP \quad (15)$$

$$S \xrightarrow{\text{light}} {}^1S^* \rightarrow {}^3S^* \quad (16)$$

$${}^3S^* \rightarrow S + \text{heat} \quad (17)$$

$${}^3S^* + O_2 \xrightarrow{k_{ox}} {}^1O_2 + S \quad (18)$$

$${}^1O_2 \xrightarrow{1/\tau_0} O_2 \quad (19)$$

$${}^1O_2 + A \xrightarrow{k_A} AO_2 \quad (20)$$

Because humic substances are known to be mixtures, we subdivided the sensitizers in humus solutions into two main categories: the symbol H indicates components that can transfer energy to 1,3-pentadiene as well as dioxygen, O_2, and the symbol S denotes substances that can transfer energy only to dioxygen. A brief discussion of this scheme follows. Light absorption promotes a photosensitizer molecule to its first excited singlet state $^1H^*$ or $^1S^*$. Singlet excited states, with lifetimes usually only on the order of 10 ns or less, are far too short lived to significantly interact with organic substrates or dioxygen present at the very low concentrations used in this study. Molecules in singlet states, however, decay in part by undergoing intersystem crossing to excited triplet states, $^3H^*$ or $^3S^*$, which are considerably longer lived. A variety of pathways may deactivate such triplets (eq 9–13, 17, and 18). These include decay to ground state (eq 9 and 17), energy transfer to dioxygen (eq 10 and 18) or some other interaction that quenches $^3H^*$ (eq 11), and energy transfer to the substrate cP or tP, in the natural water (eq 12 and 13), forming its triplet state T. The diene triplet decays back to a mixture of ground-state cP and tP (*22*).

Singlet molecular oxygen, $^1O_2$, the product of energy transfer to dioxygen (eq 10 and 18), is an excited form of oxygen that is a more powerful oxidant than dioxygen (*19*). It reacts rapidly with certain "acceptors", A (eq 20), often forming peroxidic products. Reactions of singlet oxygen with various substrates must compete with its decay back to ground state (eq 19). DMF is one of the most reactive of known singlet oxygen acceptors. Its photooxidation in air-saturated natural waters (*8, 12*) or in solutions of humic substances (*9*) involves the intermediacy of $^1O_2$.

The rates of the various energy-transfer processes depicted in the above scheme depend upon the concentration of the energy acceptor as well as the rate constants for the energy-transfer processes. Energy transfer occurs rapidly only when the triplet state energy of the sensitizer equals or exceeds that of the energy acceptor (*22*). The energy required to excite dioxygen to its first singlet state is only 94 kJ/mol. Thus, most triplet sensitizers that absorb only visible or UV light transfer energy to dioxygen rapidly (k_{ox} = 2×10^9 L/(mol s) in water) (*26*). On the other hand, the triplet state energy of dienes is about 250 kJ/mol, well above the energy required to excite dioxygen, and certainly more typical of the triplet energies of various organic pollutants such as polycyclic aromatic hydrocarbons and nitroaromatic compounds. Triplets capable of transferring energy to dienes also are able to rapidly transfer energy to dioxygen, but the reverse is not necessarily true.

In the following sections, we apply the concepts and the scheme discussed here to estimate the concentrations and energies of triplets in highly colored natural waters and

humus solutions exposed to light.

Near-Surface Triplet Concentrations in Natural Waters. In the photic zone of water bodies, the water is typically close to air saturated and the concentration of dioxygen (0.2–0.3 mM) is considerably higher than that of natural organic chemicals that are triplet energy acceptors. This factor, coupled with the great magnitude of the energy-transfer rate to dioxygen, indicates that most of the electronic energy that is transferred is likely to result in formation of singlet oxygen. This condition is also applicable to almost all of the experiments with DMF or the pentadiene that are discussed here. In all cases, the dioxygen concentration was at least an order of magnitude larger than the substrate concentration. With exposure of natural waters to sunlight, concentrations of triplets, $[^3H^*]$ and $[^3S^*]$, and of singlet oxygen, $[^1O_2]$, rapidly build to a steady state. It has previously been shown (*8*) that steady-state concentrations of $^1O_2$ can be computed by using eq 21 where k_s is the rate constant for the DMF

$$[^1O_2] = k_s/k_A \tag{21}$$

photooxygenation and k_A is the bimolecular rate constant for reaction of DMF with singlet oxygen. We estimate that k_A is 7.8×10^6 L/(mol s) on the basis of data in the chemical literature (*27*, *28*). It can readily be shown that, at steady state, the total concentration of triplets available for photosensitized reactions, $[^3H^*] + [^3S^*]$, is related to $[^1O_2]$ by eq 22. At 25 °C, k_{ox} is 2×10^9 L/(mol s), τ_0, the

$$[^3H^*] + [^3S^*] = \frac{[^1O_2]}{k_{ox}\tau_0[O_2]} \tag{22}$$

lifetime of $^1O_2$, is 4 μs (*27*), and $[O_2]$ is 2.5×10^{-4} mol/L in air-saturated water. The maximum concentration of triplets is thus equal approximately to $0.5[^1O_2]$.

The steady-state concentration of triplets capable of transferring energy to cP and tP can be computed by using eq 23 where k_i is the rate constant for the photoisomer-

$$[^3H^*] = k_i/k_q \tag{23}$$

ization (eq 4) and k_q is the effective rate constant for energy transfer from $^3H^*$ to diene. It is assumed that k_c and k_t (eq 12 and 13) both equal k_q, although, as discussed below, energy transfer to the trans isomer is slightly slower than to the cis isomer.

To estimate k_q, the quenching effect of another water-soluble diene, 2,4-hexadien-1-ol, on the photoisomerization of cP was quantitated. Both pentadiene and 2,4-hexadienol have the same published triplet state energies (*22*, *29*), so it is reasonable to assume that the triplets in natural waters transfer energy to both dienes at about the same rate. The well-known Stern–Volmer equation (*25*) was found to describe the quenching data with quencher concentrations in the 0.5–5.0 mM range (eq 24). In the

$$k_i(0)/k_i(Q) = 1 + k_q\tau[Q] \tag{24}$$

equation, $k_i(0)$ and $k_i(Q)$ are the rate constants in sunlight without and with the hexadienol present, respectively, τ is the effective lifetime of the various triplets that mediate the photoisomerization, and [Q] is the molar concentration of the hexadienol. Results of quenching studies in various air-saturated, aqueous solutions of dilute cP are shown in Table I. Acetophenone, a known high-energy triplet sensitizer, was included in these studies for comparison. The $k_q\tau$ values for acetophenone were larger than those observed in the humus solutions, indicating that either the lifetimes of $^3H^*$ and/or the k_q values for energy transfer from $^3H^*$ to dienol are lower than those for triplet acetophenone.

To estimate the lifetime(s) of $^3H^*$, kinetic data were obtained concerning the effects of dioxygen concentration on k_s for DMF and k_i for cP in sunlight. With no quencher present, the lifetime of a triplet τ equals $1/(k_d + k_{ox}[O_2])$, and the efficiency for formation of singlet oxygen from triplets equals $k_{ox}\tau[O_2]$. The maximum triplet lifetime with O_2 present equals $1/k_{ox}[O_2]$, or 2 μs in air-saturated water. Under these conditions, because τ is inversely proportional to $[O_2]$, the photooxygenation rate of DMF is predicted to be independent of dioxygen concentration, and the photoisomerization rate of cP is predicted to be inversely proportional to dioxygen concentration. Thus, as shown in Table II, the pronounced reduction in k_i and lack of change in k_s for the DMF reaction in going from air-saturated to oxygen-saturated solutions strongly indicates that the lifetimes of most of the triplets are about 2 μs.

Assuming that τ equals 2 μs, we computed k_q values for the systems in Table I. A k_q value of 2.8×10^9 L/(mol s) was computed for quenching of triplet acetophenone by hexadienol, in excellent agreement with the literature value (*29*). This result indicates that acetophenone transfers energy to dienes at the maximum possible rate in water, a result that is expected (*22*) when the energy of the sensitizer (305 kJ/mol for acetophenone) exceeds that of the diene (251 kJ/mol). Triplet energy transfer from the humic substances to dienes was also very rapid (Table I), although it was not quite as fast as with acetophenone as sensitizer. This result suggests that, on the average, triplet energy transfer from humic substances to the dienes is slightly endothermic (*22*), in agreement with the results in the following section.

The various kinetic parameters and equations that are discussed above were used to estimate typical near-surface concentrations of singlet oxygen and triplet states in the sunlight-exposed solutions (Table III). These calculations indicate that up to half of the triplets capable of transferring energy to dioxygen can also transfer it to the much higher energy dienes. On the average $[^3H^*]/([^3S^*] + [^3H^*])$ is 0.35. The rate constants for these photosensitized reactions are proportional to the UV absorption coefficients of the colored natural waters and humus solutions. For these waters the mean ratios of steady-state concentrations to the absorption coefficient at 365 nm equals 8×10^{-15} mol/(L m) for $[^1O_2]$, and 1.5×10^{-15} for $[^3H^*]$. The absorption coefficient used for these calculations was defined as 2.303 times the absorbance at 365 nm/M. Using known absorption coefficients of natural waters (*2*, *8*), we estimate that triplet concentrations in the photic zone range from about 10^{-15} (clear lakes) to 10^{-13} M (highly colored water bodies, e.g., swamps). Singlet oxygen concentrations are 5–6 times higher.

The steady-state concentrations in Table III (average for a full year) are estimated (*1*) for latitude 40°N (mid-United States) during the day near the surface of a water body. Action spectra for the reactions (see below) were used in conjunction with a previously described computer program (*1*) to make these estimates (*10*). Variations with latitude, season, and depth should be similar to the changes in photolysis rate constants of UV-absorbing pollutants or of solar UV irradiance that are discussed elsewhere (*1*, *2*).

Triplet Energies of Photosensitizers. Studies by Hammond et al. (*22*) of the photoisomerization of alkenes indicated that the photostationary state (PSS) depends on the triplet state energy of the photosensitizer. The data in Table IV illustrate this effect in the case of 1,3-pentadiene with several pure photosensitizers in distilled water.

Table IV. Photostationary States Reached in Sensitized Isomerization of 1,3-Pentadiene Using Pure Photosensitizers in Distilled Water

sensitizer	t_∞[a]	triplet state energy, kJ/mol
acetophenone	0.56	305
p-(trimethylammonio)-benzophenone chloride	0.56	293
naphthalene	0.60	254
naphthalene-2,6-disulfonic acid sodium salt	0.60	251
2-acetonaphthone	0.66	248
1-acetonaphthone	0.71	236

[a] Fraction *trans*-1,3-pentadiene at photostationary state using 313-nm light.

Table V. Fraction *trans*-1,3-Pentadiene at Photostationary State for Isomerization of 1,3-Pentadiene in River Water Samples and in Aqueous Solutions of Humic Substances

	sunlight	313 nm	366 nm
Aucilla River, FL	0.638	0.592	0.620
Suwannee River, FL	0.645	0.588	0.616
humus isolated from Wylde Lake, Ontario	0.635	*a*	*a*
Fluka humic acid	0.647	0.59	0.628
Aldrich humic acid	0.644	0.587	0.630
Contech fulvic acid	0.634	0.611	0.620
Ohio River fulvic acid	0.625	*a*	*a*

[a] Not determined.

These results are consistent with past studies showing that, with sensitizers having triplet energies in excess of 265 kJ/mol, the same fraction trans at PSS (t_∞) is obtained regardless of the triplet energy of the sensitizer. We find that t_∞ for pentadiene in water with high energy sensitizers (0.56) is about the same as that observed in organic solvents (*22*). When the triplet energy drops to about 250 kJ/mol, energy transfer to *trans*-1,3-pentadiene becomes slower than to the cis isomer and the PSS becomes more trans rich. The fraction trans at PSS increases sharply as the triplet energy of the photosensitizer drops from 254 to 236 kJ/mol. As discussed earlier, photostationary states were also obtained in the natural water samples and solutions of humic substances (Table V). Comparisons of the results in Table V with those in Table IV suggest that the predominant triplets in sunlight-irradiated humus solutions have energies of around 250 kJ/mol. The PSS (and thus available triplet energies) are slightly wavelength dependent, with the fraction trans lower with 313-nm light than with 366-nm light or sunlight, but are remarkably similar in all the natural water samples and solutions of humic substances. Because humic substances are mixtures, we cannot exclude the possibility that some of the triplets have energies higher than 250 kJ/mol.

Wavelength Dependence of the Photosensitized Reactions. The penetration of sunlight into natural waters depends strongly on wavelength in the UV and blue spectral region (*2*). To estimate the depth dependence of rate constants for photoreactions of pollutants in natural waters, it is necessary to have data concerning the wavelength dependence of the reactions (*1*). As a part of this study we have determined action spectra, i.e., the dependence of response functions on wavelength, for both the DMF and diene reactions. Typical results of these studies are shown in Figure 4 for Aucilla River water and a solution of a commercial, soil-derived humic acid. These action spectra are compared to the absorption spectra of the waters. Ultraviolet light (300–400 nm) is clearly most

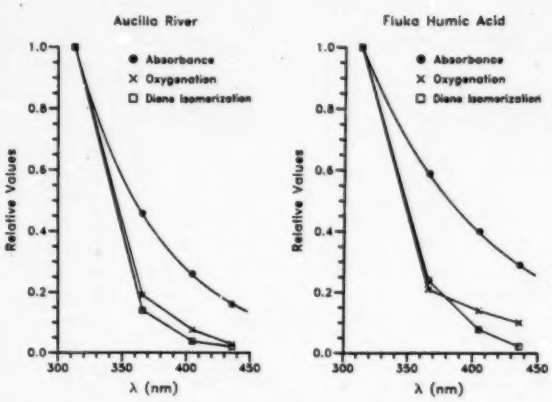

Figure 4. Comparison of action spectra for photosensitized reactions to ultraviolet–visible absorption spectra for Aucilla River water and solution of Fluka humic acid.

effective at inducing the photoreactions. There is little difference in the relative action spectra in the UV region, but in the visible region the DMF photooxygenation becomes much more efficient than the diene isomerization. This result can be explained in terms of energy-transfer considerations. The DMF reaction is mediated by energy transfer to dioxygen, whereas the diene reaction involved energy transfer to diene as the key step. As discussed above, dioxygen can accept energy from a wider variety of sensitizers, including some that absorb lower energy visible light.

It can be shown that the quantum yield for production of singlet oxygen, $Y_{s,\lambda}$, can be computed from the response function by using eq 25, where α_λ is the decadic absorption

$$Y_{s,\lambda} = \frac{X_{s,\lambda}}{2.303\alpha_\lambda k_A \tau_0} \tag{25}$$

coefficient at wavelength λ. For DMF this reduces to $Y_{s,\lambda} = (1.4 \times 10^{-4})(X_{s,\lambda}/\alpha_\lambda)$. In the near-UV region (365 nm) quantum yields in the 0.004–0.016 range were computed for the air-saturated humus solutions (see supplementary material; see paragraph at end of paper regarding supplementary material). Similar results have been reported recently by Haag and co-workers (*13*) and Baxter and Carey (*12*) with natural waters from Switzerland and Canada. The results in Table II indicate that the Y_s values closely correspond to quantum yields for the formation of triplet states.

Conclusions

The results of this study indicate that absorption of sunlight by humic substances in natural waters can lead to rapid photosensitized reactions of certain pollutants via energy transfer from molecules in their triplet states. Pollutants with triplet state energies less than 250 kJ/mol should be able to participate in these photoreactions. These chemicals include most aromatic compounds with two or more fused aromatic rings, nitroaromatic compounds, and chemicals with conjugated double bonds such as diketones and polyenes. Rates of the humus-sensitized reactions depend strongly on dioxygen concentration, indicating that the major fate of a humus triplet involves energy transfer to dioxygen to form singlet molecular oxygen. As shown in earlier studies (*9*, *19*), singlet oxygen can in turn rapidly oxidize certain substrates, including furans, sulfides, and electron-rich olefins.

Kinetic studies of photosensitized reactions in colored natural water samples and in solutions of humic substances

isolated from water bodies or soils indicated that (1) with substrates used in this study the reactions do not involve binding of the substrate by the humus (however, such binding may be significant with chemicals that strongly sorb on humus), (2) a substantial fraction (about one-third) of the humus triplets that transfer energy to dioxygen have triplet energies greater than 240 kJ/mol, (3) UV radiation is mainly responsible for inducing the photosensitized reactions, and relative action spectra for the oxygenation of DMF and the isomerization of cP were very similar in the UV region, and (4) quantum efficiencies for the production of triplets in the near-UV region fall in the 0.4–1.5% range. These conclusions provide further supporting evidence that certain commercial humic substances can be used as sensitizers that mimic the behavior of the humic substances in fresh waters.

In the upper layers of sunlit water bodies, it is estimated that typical concentrations of humus triplets with energies greater than 240 kJ/mol range from about 10^{-15} (clear lakes) to 10^{-13} M (swamps and other highly colored natural water bodies). The concentrations of singlet oxygen are estimated to be about 5–6 times higher. The rate constant of a photosensitized reaction is related to the triplet concentration by eq 26. In this equation, k_{et} is the rate

$$\text{rate constant} = k_{et}\phi_I[^3H^*] \qquad (26)$$

constant for energy transfer to substrate and ϕ_I is the probability that the product of such transfer, the substrate in its triplet state, goes on to products. The maximum values of k_{et} and ϕ_I in water are 3×10^9 L/(mol s) and unity, respectively. Therefore, average near-surface rate constants for humus-sensitized photoreactions involving triplet energy transfer in natural waters may theoretically range up to 10^{-4}–10^{-6} s^{-1} (half-lives of a few hours to several days of average sunlight).

In previous studies, it has been shown that aquatic humic substances can photosensitize reactions involving hydrogen atom transfer in addition to reactions involving energy transfer. These other photoreactions also are likely to involve triplet state intermediates, so the results of these studies can be applied to estimate environmental rate constants for these reactions as well.

These estimates, however, are based on only a few colored freshwater samples and soil-derived humus solutions. Further photochemical and flash spectroscopic research is required to determine the generality of the results reported here. In particular, recent results of Harvey et al. (*30*) indicate that the spectral properties, and thus probably the photochemical properties, of marine humus differ significantly from those of freshwater humus.

Supplementary Material Available

Derivations of the equations and a table of quantum yields for singlet oxygen production in natural water samples (5 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, author, page number) and prepayment, check or money order for $9.00 for photocopy ($11.00 foreign) or $6.00 for microfiche ($7.00 foreign), are required.

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